

## FTIR Spectroscopy

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## Biodiesel Concentration Measurements Using Attenuated Total Reflectance (ATR)

### Introduction

Reducing our dependence on fossil fuels and our reliance on oil and petroleum supplies are worldwide issues. Many see the increasing use of biodiesel fuel as a key

initiative to meet these global needs. However, the move to include proportions of biodiesel in everyday fuel has created a host of unresolved issues for both engine manufacturers and diesel consumers. Uppermost among these are questions concerning the concentration of the biofuel (Fatty Acid, Methyl Ester – FAME) and its quality. This application note describes how infrared transmission measurements can be used to address the concentration measurements.

Biodiesel fuels are often blended compositions of diesel fuel and esterified soybean oils, rapeseed oils, or other potential vegetable oils as well as fats. The physical and combustion properties of these biofuels have allowed them to achieve similar performance to diesel fuel. However, there are several characteristics (including cetane number, oxidation stability, and corrosion potential) that are of concern. These differences, especially the cetane reduction, require that adequate control of the biofuel concentration be implemented.



Figure 1: PerkinElmer Spectrum 3™

In addition, there are now tax incentives available in some parts of the world for the use of biodiesel. For example, in the USA this tax credit is presently in the form of a \$0.01 per FAME-% per gallon of fuel used. Therefore, the difference between 19% or 20% FAME in diesel fuel can result in a considerable tax value. A recent investigation of commercially available biofuel blends identified that 18 out of 50 splash-blended samples were not the specified 20% FAME value (1). It can be seen that there are financial justifications for an accurate biofuel concentration determination and characterization.

This work was performed using the Spectrum™ 100 FTIR spectrometer.\* The complete system consists of three elements:

- FTIR\* spectrometer.
- Universal ATR (UATR) plug-and-go accessory with integrated diagnostics; using a 9-bounce, liquid sampling top-plate.
- PerkinElmer® infrared quantitative software suite allowing analysis by various methodologies from Beer's Law concentration calculations using peak height measurements through to full Principal Component Analysis (PCA) chemometric analysis.

## EN method using Beer's Law

One of the few defined methods for measuring the concentration of FAME is EN 14078 (July 2014) – "Liquid petroleum products – Determination of fatty acid methyl esters (FAME) in middle distillates Infrared spectroscopy method".<sup>2</sup>

The principle of the EN method is the application of a simple quantitative model of FAME content using the 1745 cm<sup>-1</sup> carbonyl absorbance. When using the EN methods, samples are diluted in cyclohexane to a final analysis concentration of 0.1-1.14% FAME. This produces a carbonyl peak intensity range between 0.1-1.1 Abs, using a 0.5-mm cell pathlength. The peak height of the carbonyl band at or near 1745 cm<sup>-1</sup> is measured to a baseline drawn between 1820 and 1670 cm<sup>-1</sup>. This peak height is used with a Beer's Law plot (absorbance versus concentration) to develop the calibration curve used for calculating the unknown concentrations.

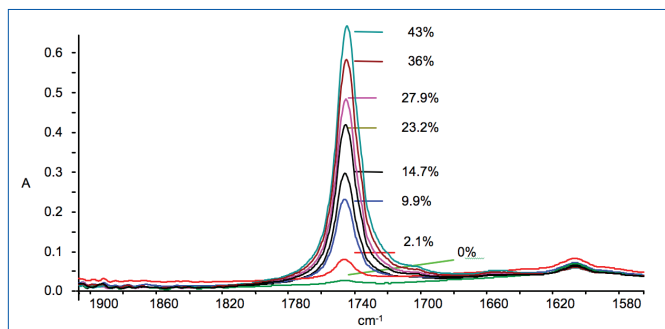


Figure 1. FTIR spectra of varying FAME concentrations in diesel fuel.

\* The Spectrum 100 is superseded by the PerkinElmer Frontier and Spectrum 3 system.

While it is possible to achieve good concentration measurement, the disadvantages of this method are the need for sample dilution and the inability of the simple methodology to cope with variances in the source of the biofuel. An improved solution, like ASTM® D7371-14, utilizes ATR to reduce the effective pathlength and avoid the sample dilution errors. As there is a potentially increasing variance in chemistry of the sources of the FAME (namely soybean, rapeseed, or yellow-grease), peak area is proposed as a preferred calculation technique.

## Beer's Law method

This method used the 9-bounce UATR to analyze the FAME content of a biodiesel sample. The method that was employed in this study included:

- Peak area calculation – range: 1820-1670 cm<sup>-1</sup> with baseline set at the same range.
- No dilution – samples were not diluted.

Since one is determining a peak area within the Beer's Law experiment to be a valid method, the peak maximum cannot exceed the detector linearity range. Figure 1 shows the spectra for 1900 to 1600 cm<sup>-1</sup> of a series of varying concentration biofuel (FAME).

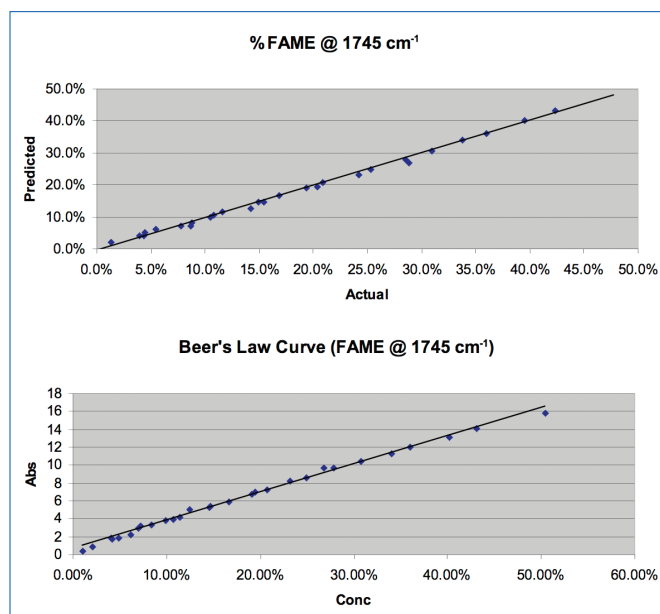


Figure 2. Beer's Law calibration method for 1745 cm<sup>-1</sup> peak.

Figure 1 demonstrates that a Beer's Law curve is possible for this spectral region to above 43% FAME. A Beer's Law method was developed for these samples and is shown in Figure 2.

This Beer's Law method took a baseline as defined in the EN 14078:2014 method at 1820-1670  $\text{cm}^{-1}$  and a peak area in the same range. The sample concentration range for this method was B0 to B43 (0% to 43% FAME). The method produced a linear curve with a correlation co-efficient of 0.995. Calculating the concentration of the standards by the method yielded a Pearson's correlation of 0.998 and a standard error of prediction (SEP) of 1.2%. These results show that this method is somewhat marginal for the quantitation of FAME.

### Chemometric method

Chemometrics application using Principal Component Regression (PCR) was employed to determine the FAME concentrations between 0 and 50% FAME. The model employed as much of the entire spectrum (4000-650  $\text{cm}^{-1}$ ) as possible. Since the sampling technique used for these analyses was the 9-bounce UATR, there is a region of high absorbance in the spectrum that is associated with the diamond (2495-1822  $\text{cm}^{-1}$ ). This region needed to be blanked from the PCR model as it just adds to the noise of the model. This method utilized only one principal component. The spectrum of this principal component, referred as the Regression Spectrum, is shown in Figure 3. It shows that there are features of both the FAME (1745 and 1170  $\text{cm}^{-1}$ ) and the diesel fuel (3012, 1605 and 810  $\text{cm}^{-1}$ ) contributing to the analyses.

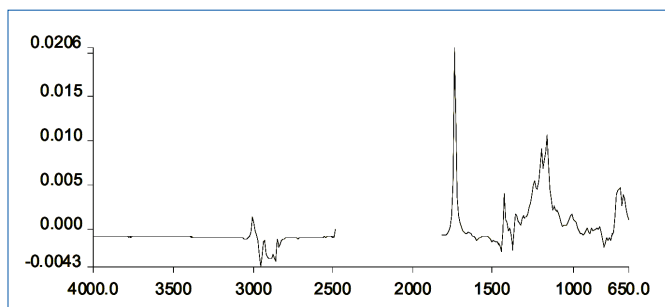


Figure 3. Biodiesel FAME concentration – PCR regression spectrum.

The statistics of this model showed a correlation coefficient of 0.9996 and a standard error of prediction (SEP) of 0.4%. The actual against predicted results for this model is shown in Figure 4; also indicating a good prediction model.

This chemometric approach to the analyses is much better than the Beer's Law method. Building a PCR model can be more difficult than Beer's Law; however, PCR does allow better statistics to tell if the results are consistent with the development standards.

### Conclusion

We have shown how the ATR technique can be used to address FAME concentration measurements. The preferred methodology uses chemometrics to analyze the whole spectrum, achieving a standard error of prediction of 0.4%. This compares well with the concentration measurement of FAME in a typical "splash blend" operation, where an error of 0.5% is usually acceptable.

FAME concentration determination is possible using both the PerkinElmer Spectrum 3 and Spectrum Two FTIR systems. A key advantage of using an ATR sampling method is speed and simplicity. This can really help in laboratories where multiple analyses are routinely performed. The choice of either Beer's Law or chemometrics will be determined by the particular situation. The Beer's Law approach benefits from being simpler but is only recommended for situations where there is a low throughput of samples and the accuracy requirements aren't high. The chemometrics approach has the advantage of being more robust with respect to known constituents in the blend, better handling of interferences, and reduced effect from noise contributions. Overall, PCR offers far higher confidence in the quantitative prediction than is found using the Beer's Law methods.

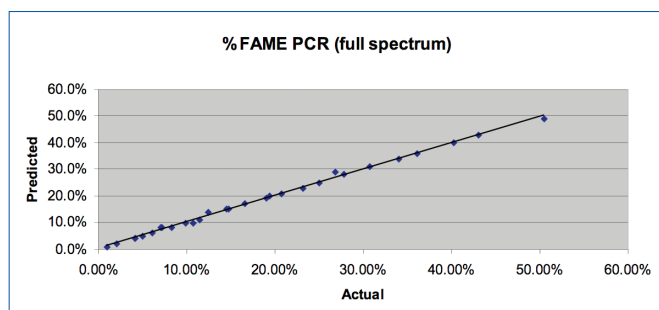


Figure 4. PCR calibration method.

## References

1. NREL Technical Report TP-540-38836, Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004; R.L. McCormick, T.L. Alleman, M. Ratcliff, L. Moens, and R. Lawrence, (October 2005).
2. EN 14078:2014 Liquid Petroleum Products – Determination of Fatty Acid Methyl Esters (FAME) in Middle Distillates – Infrared Spectroscopy Method (July 2004).
3. ASTM D7371-14 Standard Test Method for “Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy”.

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